



Cyclic voltammetric study of zinc and zinc oxide electrodes in 5.3 M KOH

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Abstract

The behaviour of zinc and zinc oxide in 5.3 M KOH in the presence of alkaline earth oxides, SnO, Ni(OH)₂ and Co(OH)₂ was examined by cyclic voltammetry. The influence of the alkaline earth oxides was compared with additives of established effects (Bi₂O₃, LiOH, Na₂CO₃ and CdO). The alkaline earth oxide each exhibits a distinct behaviour towards zincate. Whereas, a single process of interaction with zincate was shown by CaO; two modes of reaction were obtained with SrO and BaO. Solid solution formation was noticed with BeO and MgO. The other additives forming solid solution with ZnO were CdO, SnO. The ionic sizes of Ni(OH)₂ and Co(OH)₂ allow solid solution formation with Zn(OH)₂. Both Bi₂O₃ and Na₂CO₃ enter into complexation with zincate. LiOH forms two distinct zincates, of which one is an oxo zincate leaching the 'hydroxyl' functionality. Cyclic voltammetry revealed the deposition of the oxide/hydroxide additives as metal prior to the onset of zinc deposition and the potential range for this additive metal deposition is almost the same for different additives (SnO, CdO, Ni(OH)₂). The beneficial action of these additives to zinc alkaline cells is associated with a substrate effect. The implication of this electrocatalytic deposition of metals on a zinc oxide electrode is also discussed.

1. Introduction

One method of improving the cycle life of zinc alkaline cells [1] is to incorporate inorganic additives [2–6] in the electrolyte. Reactions at the zinc electrode are characterized by both chemical and electrochemical changes and are heterogeneous in nature. Despite the apparent simplicity of the reaction, the mechanism of the overall process is complex and often involves several steps [2, 7]. The technique of cyclic voltammetry is employed in the present study to examine the dissolution and deposition of zinc from zincate in the presence of inorganic additives using practical battery electrolyte (5.3 M KOH).

2. Experimental details

The same experimental details as described elsewhere [8] were applied for the preparation of reagents and solutions. Cyclic voltammetric studies were made using a home made single compartment cell of 0.1 m inner diameter with a fused-in Pt foil of large surface area as counter electrode. The working electrode was a pure Zn metal (99.99%) rod (2×10^{-4} m diameter) embedded

horizontally on a Teflon mount. This electrode was polished with emery paper (4–0 grade), degreased with acetone and finally washed with triple distilled water. The experimental solutions were deaerated by passing oxygen-free nitrogen gas through them. The measurements were made at 25 ± 2 °C using a BAS 100 A electrochemical analyzer. Cyclic voltammograms of pasted zinc electrode material were made by compacting finely ground zinc oxide (with or without the additive) mixed with a drop of PTFE binder, on either side of a silver expanded mesh, using a die in a hydraulic press. A compaction pressure of 3.5×10^4 kg m⁻² was used. The specifications of the zinc paste electrode are as follows: dimensions: 0.01 m × 0.01 m × 0.005 m; ZnO content: 3×10^{-4} kg. The reference electrode for cyclic voltammetric studies was Hg/HgO (1 M KOH) and all potentials are referred to this electrode.

3. Results and discussion

3.1. Cyclic voltammetry of zinc electrode

A typical cyclic voltammogram of zinc in 5.3 M KOH is shown in Figure 1. Starting at –1800 mV, an anodic

peak A appears in the potential range from -950 to -1025 mV. There is a sharp fall in current following attainment of the peak. During the negative sweep, an anodic current peak (designated as A_1) appears at a potential slightly negative to peak A and a cathodic peak C appears between -1450 and -1540 mV. The effect of additives are described below.

3.1.1. Influence of CaO, SrO and BaO

In the presence of CaO, there is not much change in the cyclic voltammetric pattern of zinc in 5.3 M KOH, except that peak A_1 is smaller and peak A is drawn out towards less negative potentials (Figure 1). The behaviour of SrO (Figure 1) is very similar to that of CaO except that the peaks A and A_1 are slightly more drawn out. Peak C is slightly shifted negatively (Figure 1) and i_{pA_1} and i_{pC} are less than that for CaO. The influences of SrO and CaO are very prominent in the case of BaO (Figure 1) i_{pC} is much less. At low sweep rates, SrO and BaO exhibit two anodic dissolution processes (Figure 1), whereas CaO shows only a single process. CaO, BaO and SrO are alkaline earth oxides and have a common feature, that is, all are capable of forming zincate compounds. For instance, calcium oxide forms calcium zincate, $\text{Ca}[\text{Zn}(\text{OH})_3]_2 \cdot 2\text{H}_2\text{O}$ [10, 11]. Barium oxide forms at least two zincates. $\text{Ba}[\text{Zn}(\text{OH})_4]$ and $\text{Ba}_2[\text{Zn}(\text{OH})_6]$. Strontium oxide also forms two zincates $\text{Sr}[\text{Zn}(\text{OH})_4]\text{H}_2\text{O}$, $\text{Sr}_2[\text{Zn}(\text{OH})_6]$ [12–14]. Cyclic voltammetry of the zinc electrode in the presence of these

additives at low sweep rates has clearly shown that BaO and SrO differ from CaO (Figure 2) by the appearance of shoulders in peaks A and A_1 . This distinction may be attributed to a difference in the chemical reactivity between CaO and BaO and SrO. For instance, BaO and SrO can form solid solutions with zinc oxide and other metal oxides [15–18] whereas CaO forms only zincates.

3.1.2. Influence of BeO, MgO, SnO, CdO, Ni(OH)₂ and Co(OH)₂

These additives are similar in their influence on the cyclic voltammetric behaviour of Zn in 5.3 M KOH (Figure 3). When compared with the cyclic voltammogram of zinc in plain 5.3 M KOH, i_{pA} is higher whereas i_{pA_1} is less and i_{pC} is higher. A point of interest in the additive effect of these compounds is in the slow sweep rates (Figure 4). An additional peak (indicated by the arrow) appears at about -700 mV vs Hg/HgO in all cases. This peak may be attributed to the metal deposition owing to the reduction of the additive oxides. The distinct feature of this group of additives is that they form solid solutions with ZnO, as discussed below.

ZnO has a hexagonal (Wurtzite) lattice with the following cell parameters: $a = 0.324$ nm, $c = 0.519$ nm. Among the commonly occurring metal oxides, only beryllium oxide, BeO has a hexagonal structure. Its lattice parameters are $a = 0.269$ nm, $c = 0.430$ nm. Even though the difference between the sets of parameters is somewhat greater than 15%, BeO and ZnO apparently form a solid solution, as confirmed by conductivity and X-ray diffraction measurements [19]. In the present context of solid solution formation, it is worth mentioning that coprecipitation and hydrolytic synthesis have gained importance as preparation techniques of solid solutions [20, 21]. Diadochy rather than

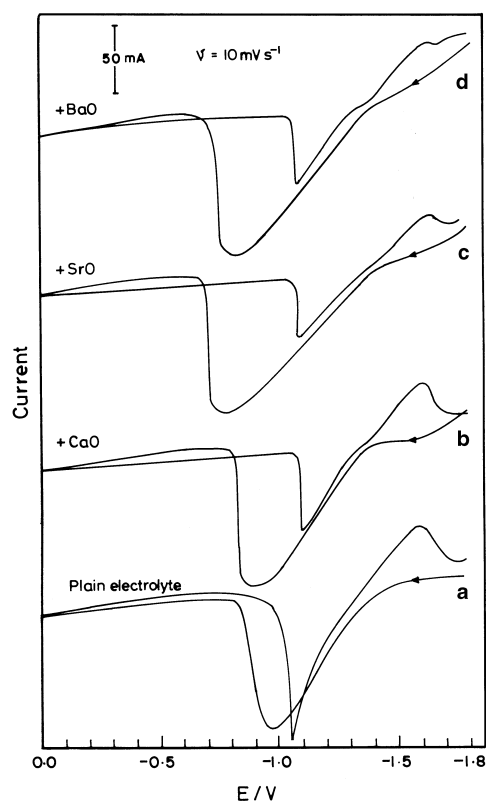


Fig. 1. Cyclic voltammogram of zinc (a) in 5.3 M KOH at a sweep rate of 30 mV s^{-1} and in presence of (b) 1×10^{-3} M CaO, (c) BaO and (d) SrO. Sweep rate 10 mV s^{-1} .

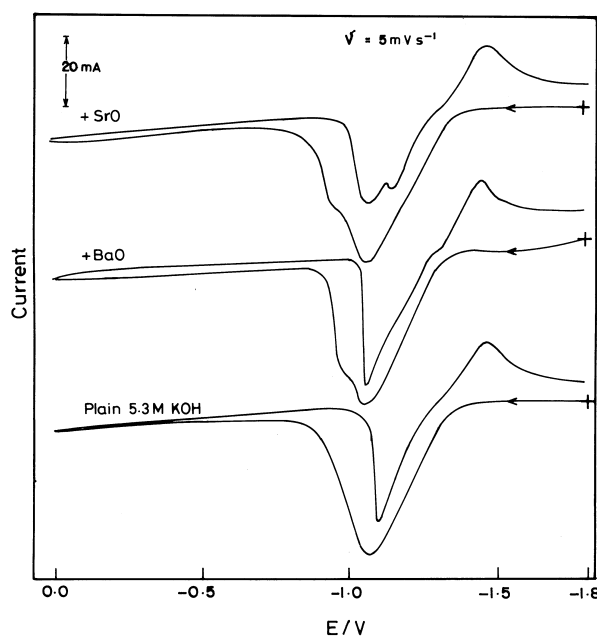


Fig. 2. Cyclic voltammogram of zinc in 5.3 M KOH in presence of (a) 1×10^{-3} M BaO and (b) 1×10^{-3} M SrO; sweep rate 5 mV s^{-1} .

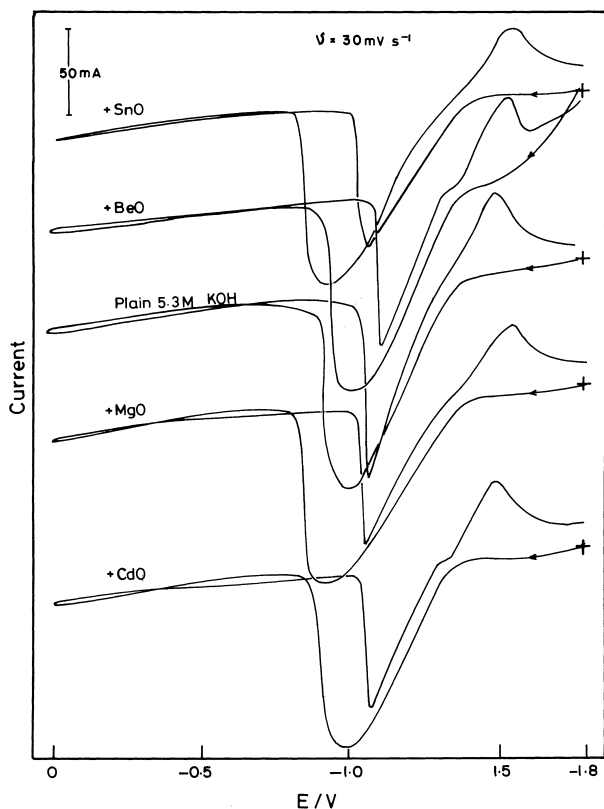


Fig. 3. Cyclic voltammogram of zinc in 5.3 M KOH in presence of (a) 1×10^{-3} M CdO, (b) 1×10^{-3} M MgO, (c) 1×10^{-3} M BeO and (d) 1×10^{-3} M SnO at a sweep rate of 5 mV s^{-1} .

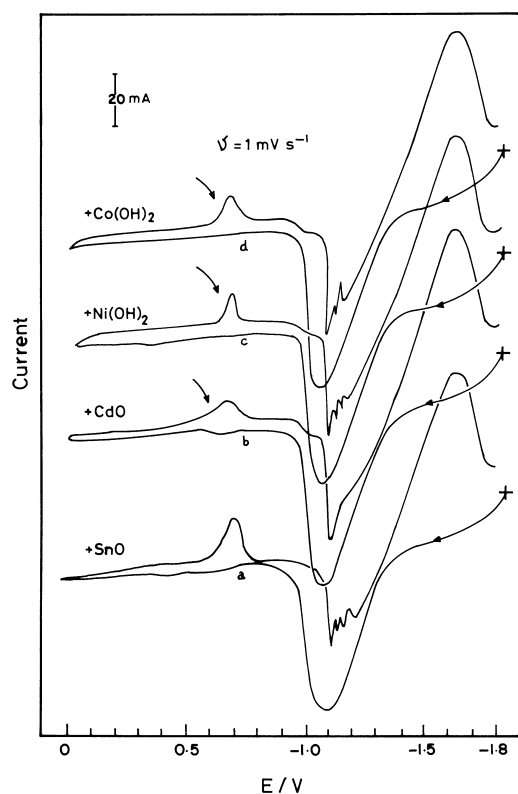


Fig. 4. Cyclic voltammogram of zinc in 5.3 M KOH in presence of (a) 3×10^{-3} M SnO (b) 1×10^{-3} M CdO (c) 1×10^{-3} M Ni(OH)₂ and (d) 1×10^{-3} M Co(OH)₂; sweep rate 1 mV s^{-1} .

isomorphism is the primary criterion in solid solution formation so that a hexagonal compound may form a solid solution with a non-hexagonal one if the ionic sizes are appropriate [22]. Substitution of one cation for another in a particular lattice is often possible if the difference in the ion sizes is less than about 15%. Using this criterion, and Pauling's empirical values for crystal radii [23], the following ions may be diadochic in oxide structures Zn: 0.074 nm; Co: 0.074 nm; Ni: 0.072 nm. This is also born out by the fact that in minerals zinc ion is often replaced by these ions. The crystal structure and cell parameters of the oxides of these metals are as follows CoO: cubic $a = 0.425 \text{ nm}$, NiO: cubic, 0.417 nm . Information available in the literature suggests that Ni(OH)₂ and Co(OH)₂ are excellent host lattices for Zn(OH)₂ [24].

3.1.3. Influence of LiOH

In the cyclic voltammogram (Figure 5) LiOH exhibited two anodic dissolution processes. One of the processes was common with the single dissolution process exhibited by most of the other additives, whereas an additional process was revealed at more negative potential ($E_p = -1375 \text{ mV}$). Therefore, the anodic dissolution products of both the processes were separately collected and analysed by IR spectra [25]. The IR spectrum of the product collected at -1375 mV , in the case of LiOH additive did not show any frequency characteristic of the hydroxide or hydroxo complexes. In contrast, a strong absorption at 1209 cm^{-1} was observed together with a strong absorption in the far IR region at 120 cm^{-1} . Generally oxide lattices show absorption around 1000 cm^{-1} and $100 - 120 \text{ cm}^{-1}$ [25]. Therefore, this product obtained from LiOH could be an oxide. Literature evidence [27] shows that lithium can, in fact, form lithium oxozincate for instance KLiZnO_2 . Such a compound, though a zincate in terminology, lacks OH functionality. Yet another zincate viz., $\text{Li}_2[\text{ZnO}_4]$ is also known [28]. Therefore, either of these compounds may be formed at -1375 mV .

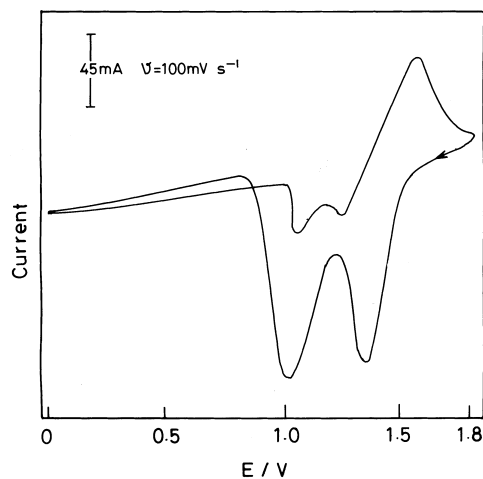


Fig. 5. Cyclic voltammogram for zinc in 5.3 M KOH in presence of 1×10^{-3} M LiOH. Sweep rate 100 mV s^{-1} .

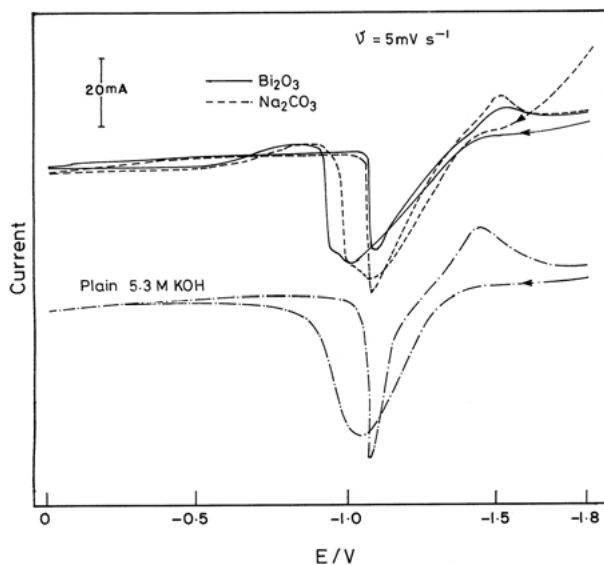


Fig. 6. Cyclic voltammogram for zinc in 5.3 M KOH in presence of 1×10^{-4} M Bi₂O₃ (—), Na₂CO₃ (---). Sweep rate 5 mV s⁻¹.

3.1.4. Influence of Bi₂O₃ and Na₂CO₃

The change brought about by these additives in the cyclic voltammogram of zinc combines the features of MgO and CaO (Figure 6). i_{pA1} is smaller and more drawn out. The behaviour of zinc in Na₂CO₃ containing 5.3 M KOH is similar to that of zinc in K₂CO₃ [29]. Turbidimetric, IR and Raman spectral analyses have proven that Bi₂O₃ and Na₂CO₃ enter into complexation with zincate [25].

3.2. Cyclic voltammetry of the zinc oxide electrode

To gain an understanding of the effect of the additives on a porous zinc electrode the cyclic voltammetric behaviour of the zinc oxide electrode in the presence of these additives was studied.

Cyclic voltammetric parameters, that is, peak potential, peak current, area covered under the peak and changes in area of the peak due to multiple cycling can aid the understanding of performance of zinc based secondary batteries.

An additive that catalyses the dissolution of zinc will shift the E_{pA} to more positive values and will aid the discharge process of conversion of zinc to zincate. An additive that aids the charge process will shift E_{pC} to less negative values. An indication of dissolution of zinc oxide is provided by i_{pA} . An indication of quantity of electroactive species for reduction is provided by i_{pC} .

The area covered under the cyclic voltammetric peak can be taken to represent the capacity of an electrode because the product of current and time is the quantity of electricity which is the 'charge' capacity of the electrode. The ordinate (y axis) of the cyclic voltammogram is i , the abscissa (x axis), although representing potential, is a time scale governed by the chosen sweep rate.

In cyclic voltammetry, a positive or negative sweep followed by a sweep in the opposite direction constitutes a cycle. This cycle may be visualized as a cycle of a secondary battery constituting a single charge and discharge.

Charge retention in a battery is reflected in the Ah capacity of the battery over repeated cycling. Batteries of practical importance have appreciable resistance to loss in capacity due to cycling. If a multiple cyclic voltammogram indicates only slight changes in area after several cycles, it is assumed to represent a good cycle life and in such systems the electrochemical reaction can be said to occur steadily.

The cyclic voltammogram of zinc oxide shows a peak at -1770 mV on the positive going sweep and a corresponding peak at -1470 mV on the negative going sweep. The peaks correspond to the anodic dissolution

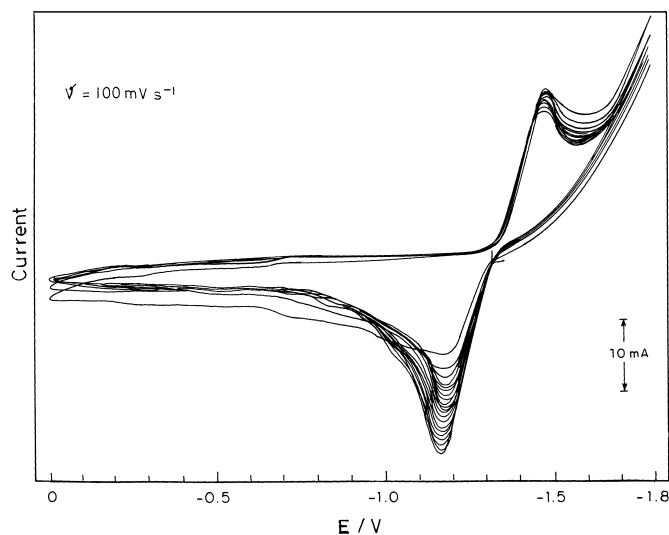
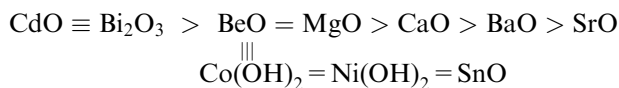


Fig. 7. Cyclic voltammogram of ZnO in 5.3 M KOH. Sweep rate 100 mV s⁻¹.

of zinc oxide and reduction of zincate, respectively (Figure 7). The cyclic voltammograms of zinc oxide with additives are shown in (Figure 8(a)–(c)).

Based on the cyclic voltammetric behaviour of zinc (Table 1) the additives can be arranged in the following order of their beneficial additive action:



Further, a distinction may be made from a comparison of the cyclic voltammetry of the zinc electrode and that of the zinc oxide electrode. LiOH and Na₂CO₃ may be more useful as additives to the electrolyte than electrode additives. This is owing to their free solubility. Bismuth oxide, however, which is freely soluble in the electrolyte, may also function as an additive to the electrode [30], since zinc can be deposited on bismuth during discharge, which provides the conductive matrix for facile electrochemical processes to take place. The same concept is revealed by the cyclic voltammogram of zinc oxide in the presence of Bi₂O₃ (Figure 6). The behaviour of CdO (Figure 8(b) and 8(c)) is similar to that of Bi₂O₃. The arrow indicates the metal deposition region of the additive.

It should be noted that the potential of metal deposition is almost the same for Bi₂O₃, CdO, MgO, SnO, BeO, Ni(OH)₂ and Co(OH)₂. This unique behaviour of additives to the zinc electrode was reported earlier by McBreen and Gannon [31], who observed quantitative deposition of oxide additive as metal prior to the onset of zinc deposition. McBreen [32] states: "it is difficult to envision how an additive of limited solubility can be quantitatively reduced in a nonconducting matrix such as ZnO. The fact that this occurs and that the effect of the additive effect may be a substrate effect that controls zinc nucleation and morphology". Formation of a conductive matrix is certainly an advantages factor for battery performance. A separate study [33] from our laboratory has shown that the nucleation and morphology of zinc electrodeposited from a zincate electrolyte is controlled by these additives. Battery discharge studies [34] supported the substrate effect of CdO as an additive to ZnO. It seems therefore reasonable to analyse the solute behaviour of ZnO/Zn(OH)₂ in an alkaline electrolyte. The semiconducting and electronic property of zinc oxide in an aqueous environment under the influence of an electric field needs to be investigated in detail. It is worth mentioned that recent years have seen renewed enthusiasm in research of zinc oxide as a photonic and an electrocatalytic material [35–38]. The observation made in the present study that is, reduction of metal oxides to metals in a zinc oxide matrix, indicates scope for future work on electrochemical reclamation of metals from their oxides.

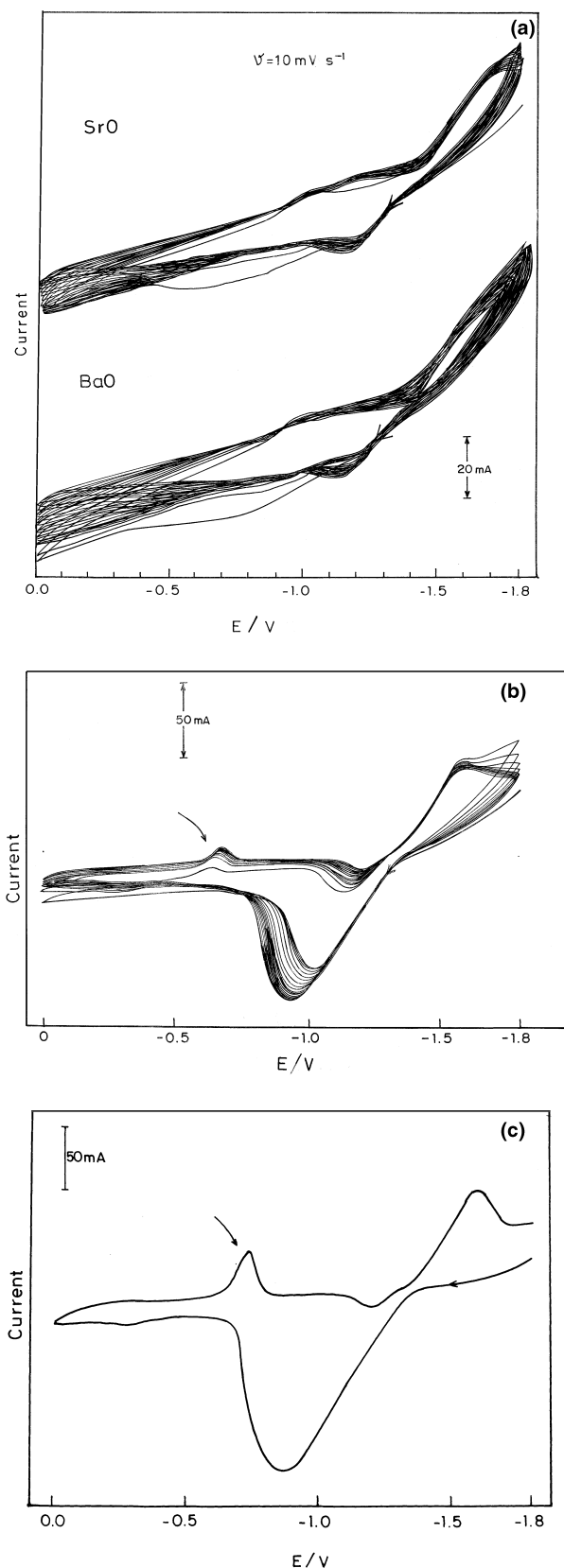


Fig. 8. (a) Cyclic voltammogram of ZnO containing 10 wt% SrO and 10% BaO in 5.3 M KOH. Sweep rate 10 mV s⁻¹. (b) Cyclic voltammogram of ZnO containing 10 wt% CdO in 5.3 M KOH. Sweep rate 10 mV s⁻¹. (c) Cyclic voltammogram of ZnO containing 10 wt% Bi₂O₃ in 5.3 M KOH. Sweep rate 10 mV s⁻¹.

Table 1. A comparative look at the cyclic voltammetric behaviour of additives incorporated into the zinc oxide electrode

Additive	Peak A	Peak C	i_{pA} comparison	i_{pC}	Shift in E_{pA}	E_{pC} Shift	Charge retention
CdO	symm broad	symm broad	equal	more	+ve	+ve	excellent
SnO	symm broad	symm broad	equal	more	nil	-ve	moderate
Bi ₂ O ₃	symm very broad	symm very broad	more	more	+ve	-ve	excellent
BeO	symm broad	symm broad	nil	more	+ve	nil	excellent
MgO	symm broad	symm broad	less	more	+ve	+ve	good
Co(OH) ₂	symm broad	symm broad	less	more	+ve	+ve	moderate
Ni(OH) ₂	symm very broad	symm broad	less	more	+ve	+ve	moderate
CaO	drawn out broad	symm broad	less ²	less ²	+ve	+ve	good
SrO	very drawn out	drawn out	less ³	less ³	-ve ¹	-ve ¹	poor
BaO	very drawn out	very drawn out	less ⁴	less ⁴	-ve ²	-ve ²	poor

Legend: symm symmetrical; less¹ peak current slightly more less than that for KOH; less² < less¹; less³ < less²; less⁴ < less³; excellent 10–15% capacity less in 30–40 cycles; good 20–25% capacity less in 30–40 cycles; moderate 30–35% capacity less in 30–40 cycles; +ve slight positive shift; -ve very slight negative shift; -ve¹ slight negative shift; -ve² > -ve¹

4. Conclusion

This study has aided understanding of the events underlying the battery discharge behaviour of Zn/ZnO in the presence of various oxides as additives. BeO, SnO, CdO, Ni(OH)₂, MgO and Co(OH)₂ form solid solutions with zinc oxide and exhibit similar cyclic voltammetric behaviour. CaO, BaO and SrO form zincates. However, BaO and SrO behave similarly while CaO behaves differently. A comparison has been made with additives of established additive action. As far as the zincate analysis is concerned, cyclic voltammetry can be ranked along with IR and Raman spectral techniques in unraveling the mode of additive action [25].

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